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Poly(4-hexyloxythiazole): A new low band gap semiconductor for polymer electronics

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ABSTRACT

A novel semiconducting polymer poly(4-hexyloxythiazole) with a low optical band gap of 1.4 eV was synthesized and used in organic electronic devices. X-ray diffraction (XRD) measurements reveal a high degree of crystallinity and lamellar packing of poly(4-hexyloxythiazole) in the film similar to poly(3-hexylthiophene). Field effect transistor charge mobility of poly(4-hexyloxythiazole) arrived 0.02 cm^2/V s. Bulk heterojunction type solar cells based on poly(4-hexyloxythiazole) shows a photoresponse up to about 900 nm.

1. Introduction

Semiconducting polymers have attracted much attention in the past decades because of their potential applications in low-cost and large-area electronic devices produced by simple painting or printing techniques on flexible substrates [1–3]. Among these polymers, regioregular poly(3-hexylthiophene) (P3HT) is one of the most extensively studied conjugated polymers because of its superior electronic properties in various devices [4–7]. Owing to the highly regular head-to-tail connectivity of the 3HT monomers, P3HT has high crystallinity in the solid state, and its spin-coated films often form a lamellar structure with the thiophene rings and the alkyl chains oriented perpendicular to the substrate [8]. This orientation is advantageous for charge transport in the lateral direction. As a result, charge carrier mobilities of up to 0.2 $cm^2\ V^{-1}\ s^{-1}$ have been achieved for P3HT-based organic field effect transistors (FETs) [9–12]. P3HT has also been widely studied as an active material in polymer solar cells (PSCs) and photodetectors [6,7,13,14]. P3HT-based PSCs have remarkably high fill factors, which can be attributed to the high crystallinity and the high charge carrier mobility of P3HT. PSCs based on P3HT, however, utilize only photons with wavelengths below 650 nm, which limits photovoltaic performance.

Various low band gap polymers have recently been extensively studied for application to PSCs and ambipolar FETs [15–21]. For PSCs, it is highly desirable to combine high charge carrier mobility with long-wavelength absorption to achieve high photocurrent. For ambipolar FETs, small band gap are necessary for efficient electron and hole injection from the same electrode. One promising strategy for designing such polymers would be to start from regioregular P3HT and modifying the energy levels of the polymers while maintaining the highly ordered structure. To reduce the band gap of the poly(3-alkylthiophene) analogs, the incorporation of electron-donating groups such as alkoxy groups at the 3-position of the thiophene ring has been reported [22–24]. Although the band gap of the polymer was reduced substantially, the electron-donating effect of the alkoxy group raised the level of the polymer's highest occupied molecular orbital (HOMO) by 0.3–0.5 eV and also lowest unoccupied molecular orbital (LUMO) [23,24]. This makes the resulting polymer easily doped with oxygen in the air, and therefore it is difficult to use the polymer in actual electronic devices.

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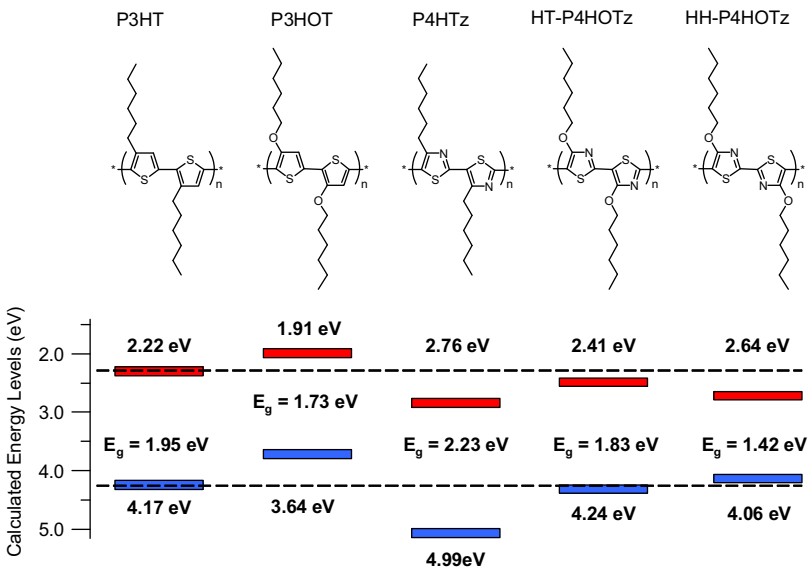


Fig. 1. Calculated energy levels for poly(3-hexylthiophene) (P3HT), poly(3-hexyloxythiophene) (P3HOT), poly(4-hexylthiazole) (P4HTz), head-to-tail and head-to-head poly(4-hexyloxythiazole) (P4HOTz).

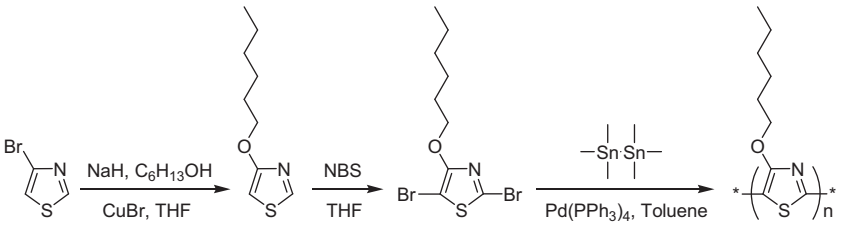
Furthermore, the high HOMO level of the donor materials will cause a low open circuit voltage in PSCs, thus limiting the overall efficiency. Recently, Heeney et al. reported the design and synthesis of regioregular poly(3-hexylselenophene) (P3HSe), in which the sulfur atom of P3HT was replaced with selenium in the polymer backbone [25]. This polymer has a lower band gap compared with P3HT because the ionization potential of selenium is smaller than that of sulfur, and the HOMO level is not notably changed. Owing to the structural similarity to P3HT, P3HSe has shown high hole mobility in an FET and moderate photovoltaic performance in a PSC [25,26].

In the present study, we use a building block of thiazole, in which one carbon of a thiophene ring is replaced with nitrogen. It is known that the thiazole unit is electron-deficient compared with thiophene; therefore, the homopolymer of thiazole should have deeper HOMO and LUMO levels compared with polythiophene. The synthesis, structure study and the applications in light-emitting diode of polyalkylthiazole have been reported by several pioneering groups [27–36]. Very recently, Pammer et al. also reported the first head-to-tail regioregular polyalkylthiazole by using Kumada-coupling polycondensation [37]. They had shown that the regioregular polythiazole has a 0.3–0.5 eV deeper HOMO level and a similar bandgap compared with regioregular poly(3-alkylthiophene). Introduction of electron-donating side chains to polythiazole could lead to a low band gap polymer without significantly changing the HOMO levels compared with poly(3-alkylthiphene). Here, we report the synthesis of a novel low band gap polymer poly(4-hexyloxythiazole) (P4HOTz) and its use in organic electronic devices. We expected that P4HOTz would also have good crystallinity and electronic properties due to its structural similarity to P3HT.

2. Results and discussion

To predict the optoelectronic properties of the new polymer, theoretical calculations were conducted by using density functional theory (DFT) under periodic boundary conditions (PBCs) with the B3LYP functional and the 6-31G(d) basis set. The calculated energy levels for P3HT, poly(3-hexyloxythiophene) (P3HOT), poly(4-hexylthiazole) (P4HTz), and head-to-tail and head-to-head P4HOTz are shown in Fig. 1. A comparison between P3HT and P3HOT shows that the incorporation of a hexyloxy group at the 3-position of the thiophene ring leads to a smaller band gap, while both HOMO and LUMO levels are substantially raised. This result is consistent with previous studies reported by McCullough and Pei [22,23]. On the other hand, the calculated HOMO and LUMO levels of P4HTz are much deeper than those of P3HT, which is consistent with the reports by Pammar [37]. After the electron-donating alkoxy group is incorporated at the 4-position, the polymer with either head-to-tail (HT) or head-to-head (HH) structure gives smaller band gaps compared with P3HT without significantly raising the HOMO levels. These calculations predict the promising optoelectronic properties of P4HOTz for use in PSCs.

P4HOTz was synthesized as shown in Scheme 1. Starting from 4-bromothiazole, 4-hexyloxythiazole was obtained by a copper(I)-mediated substitution reaction in tetrahydrofuran (THF) [38]. It was further reacted with *N*-bromosuccinimide (NBS) in THF at room



Scheme 1. Synthetic route for P4HOTz.